

## Biomaterial Interfaces Division

### Room Union Station B - Session BI-TuP

#### Biomaterial Interfaces Posters/Flash Session

**BI-TuP1 Combining Geometry of Folded Paper with Liquid-Infused Polymer Surfaces to Concentrate and Localize Complex Solutions, Daniel Regan, C. Lilly, A. Weigang, L. White, E. LeClair, C. Howell, University of Maine**

Diagnostic devices which can provide information relevant to health and safety on-site without the requirement for a fully-equipped laboratory are of great interest for medical, military, and disaster relief applications. However, most research and development work on such devices focuses on detection rather than the preliminary sample handling and preparation. In this work, we demonstrate how low-cost paper materials coated with liquid-infused polymer surfaces can be fabricated and folded to produce shapes which result in functional sample preparation; namely, the simultaneous localization and concentration of a liquid sample. Surfaces were fabricated by infusing commercially-available silicone-release paper with a compatible polydimethylsiloxane oil to create a liquid overlayer. Adhesion tests with *Escherichia coli* on these surfaces showed no remaining bacterial cells after exposure to a sliding droplet containing  $10^8$  cells/mL, compared to the macro- and micro-scale bacterial residues remaining on the controls. Folding of the paper substrates into several 3D engineered arrays enabled clean separation of dye-containing liquids into discreet, pre-defined localized points, whereas the use of unfused controls resulted in the retention of dye on the sides. When used with a bacterial solution, the combined features of low bacterial adhesion and liquid separation via geometry resulted in the localization of a solution of *E. coli* and simultaneous concentration by 23.1 ( $\pm 6.5$ ) times, compared to only 6.78 ( $\pm 3.6$ ) times for unfused controls ( $P=0.004$ ). This work demonstrates the potential of paper-based materials with liquid-infused polymer surfaces for the manipulation and handling of complex samples which may help in the future design of on-site diagnostics.

**BI-TuP2 Photoinduced Amphiphilic Zwitterionic Carboxybetaine Polymer Coatings with Marine Antifouling Properties, Florian Victor Koschitzki, A. Rosenhahn, Ruhr-University Bochum, Germany**

Due to ecological and economic consequences, the prevention of undesirable settlement of biomass on surfaces in the marine environment is of key interest. Thus, research on effective surface-modification and application of antifouling coatings is demanded. Zwitterion containing hydrogels with stable hydration have shown promising results for ultra-low fouling materials. The spectrum of application ranges from protein and plasma resistance<sup>1</sup>, studies of bacterial adhesion<sup>2</sup>, biomedical purposes<sup>3</sup> to settlement experiments with marine biofoulers<sup>4</sup>. Although understanding the influence of anionic and cationic groups, charge distribution and charge neutrality can be discussed using self-assembled monolayers<sup>5</sup> (SAM), zwitterionic moieties must eventually be applied in the form of polymer coatings for technical purposes. To combine mechanical and antifouling properties of several materials, amphiphilic polymers are increasingly being explored.<sup>6</sup> To demonstrate the advantage of random copolymers over homopolymers regarding antifouling<sup>7</sup>, polymer coatings with varying hydrophilicity were prepared. Therefore, a carboxybetaine methacrylate was incorporated into a hydrophobic matrix via «grafting to» photoinduced radical polymerisation. Monomer solutions were applied on glass substrates, functionalized by 3-trimethoxysilyl propyl methacrylate. The samples were characterized by AFM, CA, IR and SEM. For further investigations concerning the antifouling properties, microfluidic experiments with the diatom genus *Navicula perminuta* were carried out. The results display severe enhancement of fouling prevention at small zwitterionic content of only (5 wt%).

[1] – W. Yang, H. Xue, W. Li, J. Zhang, S. Jiang, *Langmuir* **2009**, *25*, 11911-11916.

[2] – G. Cheng, G. Z. Li, H. Xue, S. F. Chen, J. D. Bryers, S. Y. Jiang, *Biomaterials* **2009**, *30*, 5234-5240.

[3] – L. Zhang, Z. Cao, T. Bai, L. Carr, J.-R. Ella-Menye, C. Irvin, B. D. Ratner, S. Jiang, *Nat Biotech* **2013**, *31*, 553-556.

[4] – S. Y. Jiang, Z. Cao, *Advanced Materials* **2009**, *21*, 1-13.

[5] – S. Bauer, J.A. Finlay, I. Thome, K. Nolte, S. C. Franco, E. Ralston, G. E. Swain, A. S. Clare, and A.

Rosenhahn, *Langmuir* **2016**, *32*, 5663.

[6] – C. Ventura, A. J. Guerin, O. El-Zubir, A. J. Ruiz-Sanchez, L. I. Dixon, K. J. Reynolds, M. L. Dale, J. Ferguson, A. Houlton, B. R. Horrocks, A. S. Clare, D. A. Fulton, *Biofouling* **2017**, *33*, 892-903.

[7] – A. L. Hook, C.-Y. Chang, J. Yang, J. Luckett, A. Cockayne, S. Atkinson, Y. Mei, R. Bayston, D.J. Irvine, R. Langer *et al.*, *Nature biotechnology* **2012**, *30*, 868.

**BI-TuP3 Peptide sequences with Ultra-Low Nonspecific Protein Adsorption and Resistance Against Marine Biofouling, Cindy Denise Beyer, M. Reback, Ruhr-University Bochum, Germany; J.A. Finlay, Newcastle University, UK; S. Gopal, Ruhr-University Bochum, Germany; A.S. Clare, Newcastle University, UK; L. Schäfer, N. Metzler-Nolte, A. Rosenhahn, Ruhr-University Bochum, Germany**

Efficient fouling-release coatings frequently consist of a silicone network modified by additional chemical compounds that reduce adhesion of marine fouling organisms. We explored the fouling-release potential of several oligopeptide sequences and tested them as self-assembled monolayers. The design motif of the peptide sequences considered inherent properties such as conformation and hydrophilicity. Different sequences were synthesized, and well-hydrated peptide coatings were assembled. All surfaces were characterized with respect to their wettability, layer thickness, and surface structure by contact angle goniometry, spectroscopic ellipsometry, and FTIR-spectroscopy. Protein adsorption of fibrinogen and lysozyme was very low on the oligopeptide SAMs. The assembled monolayers show remarkable fouling-release behavior against *Navicula perminuta* which was tested in a microfluidic assay. Also, the settlement of zoospores of the green algae *Ulva linza* was investigated. Besides the good antifouling behavior, the inclusion of Aib and D amino acids helped to create peptides that were 100% resistant against enzymatic degradation by trypsin. Due to their diversity, easy synthesis and biocompatibility, peptides could be used as active, hydrophilic components in fouling-release technologies.

**BI-TuP4 The Effect of Surface Charge and Film Hydration on the Antifouling Performance of Polyelectrolyte Multilayers, Thuvarakhan Gnanasampanthan, Ruhr University Bochum, Germany; A. Rosenhahn, Ruhr-University Bochum, Germany**

Marine biofouling, which describes the accumulation of animals, plants, and microorganisms on surfaces in the aqueous environment, causes tremendous economic and ecological concerns.<sup>[1][2]</sup> Since commonly used antifouling coatings were banned and restricted because of their toxicity, new non-toxic alternatives must be developed and established.<sup>[3]</sup> Polyelectrolyte multilayers are widely applied when protein resistance<sup>[4]</sup> and antibacterial properties<sup>[5]</sup> are required and provide a suitable platform to test the antifouling capabilities of promising compounds such as alginate (AA)<sup>[6]</sup>, chitosan (CH)<sup>[7]</sup> and polyethylenimine (PEI)<sup>[8]</sup>. The physicochemical and marine antifouling properties of chemically cross-linked alginate/chitosan- and alginate/polyethylenimine-multilayers were investigated with a focus on the influence of surface charge and film hydration. Surface plasmon resonance spectroscopy revealed that all multilayers exhibit high protein resistance. Both, positively and negatively terminated AA/PEI-multilayers did not show any differences regarding the amount of irreversibly bound protein, neither for negatively charged nor for positively charged proteins. However, for the AA/CH-coatings the charge of the terminating layer had an effect on the protein adsorption. Besides, the type of polymer within the multilayers had a strong influence on the protein resistance. Microfluidic diatom accumulation assays<sup>[9]</sup> demonstrated that all multilayers present relatively low diatom settlement and that especially for AA/PEI-multilayers the charge of the terminating layer has a significant influence on the attachment.

#### References

[1] M. P. Schultz, *Biofouling* **2007**, *23*, 331.

[2] I. B. Beech, J. Sunner, *Curr. Opin. Biotechnol.* **2004**, *15*, 181.

[3] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coat.* **2004**, *50*, 75.

[4] J. H. H. Bongaerts, J. J. Cooper-White, J. R. Stokes, *Biomacromolecules* **2009**, *10*, 1287.

[5] P.-H. Chua, K.-G. Neoh, E.-T. Kang, W. Wang, *Biomaterials* **2008**, *29*, 1412.

[6] Y. Li, J. Rodrigues, H. Tomás, *Chemical Society reviews* **2012**, *41*, 2193.

[7] O. Yemul, T. Imae, *Colloid Polym Sci* **2008**, *286*, 747.

[8] M. N.V. Ravi Kumar, *React. Funct. Polym.* **2000**, *46*, 1.

# Tuesday Evening Poster Sessions, October 22, 2019

[9] K. A. Nolte, J. Schwarze, C. D. Beyer, O. Özcan, A. Rosenhahn, *Biointerphases* **2018**, 13, 41007.

**BI-TuP5 Mass Spectrometric Determination of Active Adsorption sites of soil organic Carbon on Clay Mineral Surface, Zihua Zhu, L. Huang,** Pacific Northwest National Laboratory; *W. Liu*, China University of Geosciences, Wuhan

The heterogenic active adsorption sites on mineral surfaces may harbor critical determination on the protecting capability, preference and efficiency on soil organic carbon (SOC) components. Molecular evidence to show organic behaviors during mineral-microbe-organic interactions is urgently needed to reveal the underlying protecting-releasing mechanism for better prediction on the SOC dynamics. However, such information has been hard to obtain in the complex soil systems. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool with unique advantages to reveal systematical changes of both SOC and mineral surfaces during mineral-microbe-organic interactions. In this work, ToF-SIMS and principle component analysis (PCA) were used to study the molecular mechanisms of organic preference (e.g., humic substances vs. microbial carbon) by Fe-rich clay mineral (e.g., nontronite NAu-2) during microbial Fe redox processes. Active adsorption sites, which have only been hypothesized or computationally investigated in previous research, were successfully determined by ToF-SIMS data. Such a success indicates a bright future of extensive application of ToF-SIMS and PCA on this field.

**BI-TuP6 Blood Compatible Coating using Tethered Heparin to Reduce Coagulation in Microfluidic Devices, Ryan Faase, W. Prusinski, KS. Schilke, A. Higgins, J.E. Baio,** Oregon State University

Hyperbilirubinemia, a condition characterized by excessive bilirubin levels, affects over half of newborn babies and can lead to serious complications including brain damage or death. Absorption of light by bilirubin leads to isomerization reactions that convert bilirubin into more readily excreted compounds (e.g. lumirubin). Here, an extracorporeal microfluidic device has been developed and optimized to isomerize bilirubin in neonates, with an efficiency that exceeds the current treatment, exchange blood transfusions. The microfluidic devices are formed from cyclic olefin copolymer and the main design challenge for this device is hemocompatibility. Our approach is to modify the blood contacting channels by tethering heparin, a powerful anti-coagulant, to the surface. This is achieved by first coating the surfaces with poly(dopamine) (PDA) and then adsorbing silver nanoparticles onto the PDA layer followed by a thiol based amine terminated self-assembled monolayer (SAM). PDA provides a route for coating virtually any surface and along with silver nanoparticles the PDA-silver interface becomes antimicrobial. The SAM formed on the PDA-silver surface can be tailored for covalent linkage of the desired molecule. For this device, heparin is chemically modified, while retaining the active site, and covalently attached to the SAM with an end-on orientation to preserve activity. Heparin's potency, in terms of anti-coagulative power, comes from a heavily sulfated penta-saccharide sequence. This sequence selectively binds precursors that produce fibrinogen, the basis of a clot. Therefore, the heparin must be covalently bound in an end-on orientation to expose this penta-saccharide sequence as opposed to allowing it to adsorb to the surface. Fluorescent microscopy provides the relative coverage of available sites for heparin attachment. Fluorescein isothiocyanate is selective to primary amines and demonstrate the density of amines that can be covalently bonded with heparin. Additionally, surface density of these amine groups was confirmed by X-ray photoelectron spectroscopy. Finally, the activity of surface bound heparin is dependent on orientation with respect to the channel surface. Thus, sum frequency generation vibrational spectroscopy provides information on the tilt angle of heparin at an interface by probing S=O, C-H and O-H vibrational modes at the modified surface.

**BI-TuP7 Analysing the Sequestration of Pro-inflammatory Chemokines into Immuno-modulating Hydrogels using ToF SIMS, Nicholas Dennison, R. Zimmermann, M. Nitschke, V. Magno, U. Freudenberg, C. Werner,** Leibniz Institute of Polymer Research Dresden, Germany

Chemokines are a class of signalling molecules that play a crucial role in the wound healing process by recruiting immune cells to the affected tissue. In chronic inflammations, this physiological response is prolonged and exacerbated, ultimately causing the destruction of the inflamed tissue and, consequently, the production of more pro-inflammatory chemokines.

One way of interrupting this vicious cycle of chronic inflammations is to remove chemokines from the tissue. Our group has previously demonstrated that hydrogels based on star-shaped polyethylene glycol (starPEG) and desulfated heparin show a promising sequestration pattern

of pro-inflammatory chemokines including interleukin-8 (IL-8) and macrophage inflammatory protein-1a (MCP-1) [Lohmann et al. *Sci. Transl. Med.* **9** (2017)].

Analysis of chemokine-loaded hydrogels with time-of-flight secondary ion mass spectrometry (ToF-SIMS) and principle component analysis (PCA) of the obtained spectra allowed for further characterisation of the scavenging process. The results obtained through this methodology were integrated with the enzyme-linked immunosorbent assay (ELISA) detection technique to further optimise the immune-modulating hydrogel.

## Author Index

**Bold page numbers indicate presenter**

— B —

Baio, J.E.: BI-TuP6, 2

Beyer, C.: BI-TuP3, **1**

— C —

Clare, A.S.: BI-TuP3, 1

— D —

Dennison, N.R.: BI-TuP7, **2**

— F —

Faase, R.: BI-TuP6, **2**

Finlay, J.A.: BI-TuP3, 1

Freudenberg, U.: BI-TuP7, 2

— G —

Gnanasampanthan, T.: BI-TuP4, **1**

Gopal, S.: BI-TuP3, 1

— H —

Higgins, A.: BI-TuP6, 2

Howell, C.: BI-TuP1, 1

Huang, L.: BI-TuP5, 2

— K —

Koschitzki, F.V.: BI-TuP2, **1**

— L —

LeClair, E.: BI-TuP1, 1

Lilly, C.: BI-TuP1, 1

Liu, W.: BI-TuP5, 2

— M —

Magno, V.: BI-TuP7, 2

Metzler-Nolte, N.: BI-TuP3, 1

— N —

Nitschke, M.: BI-TuP7, 2

— P —

Prusinski, W.: BI-TuP6, 2

— R —

Reback, M.: BI-TuP3, 1

Regan, D.P.: BI-TuP1, **1**

Rosenhahn, A.: BI-TuP2, 1; BI-TuP3, 1; BI-TuP4, 1

— S —

Schäfer, L.: BI-TuP3, 1

Schilke, K.S.: BI-TuP6, 2

— W —

Weigang, A.: BI-TuP1, 1

Werner, C.: BI-TuP7, 2

White, L.: BI-TuP1, 1

— Z —

Zhu, Z.H.: BI-TuP5, **2**

Zimmermann, R.: BI-TuP7, 2